

# X-Ray Fluorescence Spectrometry

## General Use

**Qualitative.** X-ray fluorescence spectrometry (XRF) can be used to rapidly and nondestructively identify elements with atomic number ( $Z$ ) greater than fluorine. XRF limits of detection range from about 0.5 to 50 ppm, depending on the element and counting conditions. The method is especially applicable to high- $Z$  elements in a low- $Z$  matrix.

**Semiquantitative.** Semiquantitative XRF methods use semitheoretical calculations to correct for self-absorption and enhancement of the emitted x rays. This can be done without standards or with only a few standards. In the absence of considerable work, uncertainty is usually 20 to 50% of the reported value. Limits of detection are similar to qualitative work.

**Quantitative.** Quantitative analysis with XRF involves comparison of a sample with a suite of standards in a similar matrix. The standards and samples can be analyzed as received, or subjected to preparation techniques that improve the reliability of the measurement. Accuracy is generally better than 1% with good sample preparation and standardization. Quantitative analysis is difficult because the preparation of uniform solid-state standards is difficult.

## Principle of Technique

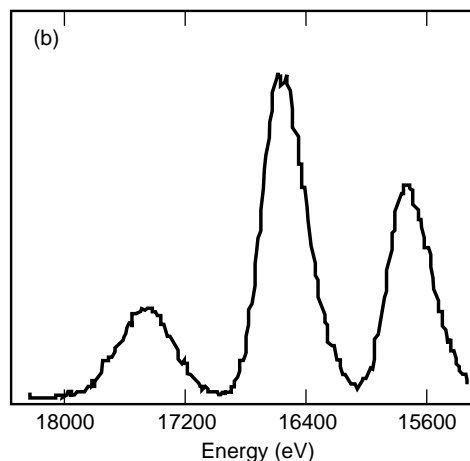
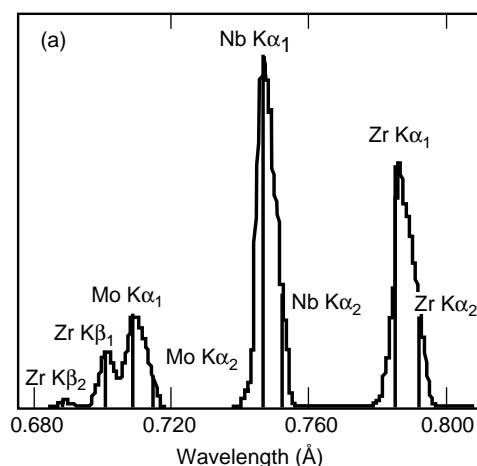
In XRF, a sample is placed in a collimated flux of high-energy photons produced by an x-ray tube. As these photons pass into a sample, some are absorbed by the inner-shell electrons of the constituents. If the photon energy is great enough, an inner-shell electron can be ejected, leaving a vacancy. An outer-shell electron will quickly fill this lower-level atomic orbital according to atomic selection

rules. In making this transition, the excess energy can be emitted as an x ray. Since the atomic energy levels are quantized and depend on the atomic number of the atom, emitted x rays form a pattern that is characteristic of each element. The energies of the observed x rays identify the element, and their intensities can, with some corrections for self-absorption or enhancement, determine the quantity of each element present.

## Samples

**Form.** Samples may be submitted as liquids, powders, or solids.

**Size.** For quantitative analysis, a minimum of about 1 g of powder, 10 mL



## Examples of Applications

- Semiquantitative analysis of unknowns.
- Determination of trace elements in equipment components.
- Qualitative analysis of surface swipes to identify materials from explosives testing.
- Identification of major elements in soil.
- Qualitative analysis of unknowns for waste disposal.
- Quantitative analysis of laser targets for the Inertial Confinement Fusion program and L Division.
- Determination of trace elements in shale oil.
- Analysis for fluorine-containing compounds on cloth.
- Measurement of impurities in materials used in the nuclear test program.

Two XRF instruments are available: (a) the wavelength dispersive XRF, which has superior resolution and sensitivity and (b) the energy dispersive XRF, which can handle odd-shaped solids. Qualitative analysis of an alloy was performed rapidly by both methods.

(H)																		(H)	(He)
(Li)	(Be)												(B)	C	N	O	F	Ne	
Na	Mg												Al	Si	P	S	Cl	Ar	
20	20												40	50	50	20	20	100	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
20	30	50	40	40	30	30	40	20	20	10	10	10	10	20	10	10	20		
Rb	Sr	Y	Zr	Nb	Mo	(Tc)	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
10	10	10	10	10	10		20	20	30	30	30	50	60	120	100	10	10		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
100	120	80	40	40	40	30	30	30	20	20	20	20	30	30					
Fr	Ra	Ac	Rf	Ha															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
50	50	50		50	60	60	40	30	30	30	30	30	30
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
20		20											

Ag  
1

← Element  
← Typical reporting limit (μg) for element in mid-z solid matrix using wavelength dispersive x-ray fluorescence spectrometer

XRF is capable of detecting all elements, but the x rays from low-Z elements ( $Z < 6, C$ ) do not have enough energy to be detected with our equipment. Elements and typical reporting limits (ppm) for a standard semiquantitative multielement scan using the wavelength dispersive instrument are highlighted. Shaded blocks indicate detection limits ( $3\sigma$ ) for careful quantitative work under optimum conditions. Detection and reporting limits depend on sample matrix and the potential presence of other elements.

of liquid, or a 1-in.-square sample of solid is required. Qualitative analysis can be performed on as little as 50 to 100 mg, although larger amounts are preferred.

**Preparation.** Frequently no preparation is required for a simple qualitative analysis. For quantitative analysis, solid samples are often fused with lithium salts and cast into plates. Some materials can be pelletized in a press to yield a suitable specimen. Occasionally solid samples can be analyzed quantitatively with virtually no preparation, and liquids are generally analyzed as received.

#### Limitations

XRF cannot be used for the analysis of hydrogen, helium, or beryllium. The detection limits are poor for other light elements, such as boron, fluorine, and sodium. XRF does not provide any information on chemical speciation or the oxidation state of elements detected (e.g., it cannot distinguish  $Fe^{2+}$  from  $Fe^{3+}$ ). Owing to the difficulty in preparing solid-state standards, precise quantitative analysis is

usually performed by other techniques. Because x rays have finite penetrating power through materials, XRF is typically used for solid samples less than several hundred microns thick.

#### Estimated Analysis Time

A complete qualitative scan of the elements requires 20 to 30 min and a semiquantitative measurement, approximately 1 h. Quantitative analysis time varies depending on the time needed for preparation of the samples and standards.

#### Capabilities of Related Techniques

DC-arc optical emission spectroscopy (DC-arc) is useful for lower-Z elements that XRF cannot detect. Sensitivities are in the ppm range. It is applicable to solid samples. Atomic absorption spectrometry and the various plasma spectrometry techniques (inductively-coupled-plasma emission spectroscopy, DC-plasma optical emission spectroscopy) are quantitative but require samples in solution. Their limits of detection for lighter elements may be more favorable than the limits of XRF.

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